

Applications of Diethoxymethane as a Versatile Process Solvent and Unique Reagent in Organic Synthesis

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Abstract:

Diethoxymethane (DEM) has recently become available in commercial quantities. It has unique properties and is useful in a variety of applications in organic synthesis. It is low boiling (88 °C), azeotropes with water, and has a very low affinity for water. It is stable under basic conditions and as manufactured does not require drying for use as a solvent, even for organometallic reactions. DEM is useful as a process solvent especially for sodium hydride reactions, organolithium chemistry, copper-catalyzed conjugate additions, and phase-transfer reactions. As such, DEM is a potential replacement for tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), glyme (1,2-dimethoxyethane), and methylal (1,1-dimethoxymethane). DEM is also useful as an ethoxymethylating agent, a formaldehyde equivalent, and a carbonylation substrate. Due to these unique properties and applications, DEM has exciting potential for widespread use both as a reagent and especially as a preferred solvent.

Background Information

Diethoxymethane is an intriguing molecule with densely packed functionality. That may be the reason that there are over 300 citations for various uses of DEM, despite the fact that it only recently became commercially available.¹ The documented uses are varied and will be briefly described to indicate the versatility of this molecule.

DEM has found use as a solvent in a number of unusual applications. For example, it has been reported to be a useful solvent in lithium batteries with nonaqueous electrolytes.^{2,3} Several diethers including DEM were found to be useful fuel additives to reduce carbon monoxide emissions and to increase octane ratings.⁴ DEM was reported to be a useful solvent for adhesives and other resins.^{5–7} In many of these

cases, DEM and other formaldehyde acetals were used as solvents and stabilizing agents since DEM can act a source of formaldehyde. Because DEM is a protected form of formaldehyde, it has been used as an attractive source of formaldehyde (instead of an aqueous solution) due to its ease of handling, safety, and nonaqueous nature. For example, several novel 6-methylene-substituted steroid derivatives with potential use as anticancer agents were prepared in good yields using DEM as a methylenating agent in the presence of phosphorus oxychloride.⁸ In addition, sterically hindered di- and trialkylphenols upon condensation with formaldehyde acetals such as DEM in the presence of an acid catalyst afforded dimers (bisphenols) and oligomers (polyphenols) useful as nontoxic, colorless, low volatility antioxidants for rubbers and plastics.⁹ Bis(phenylcarbamate) esters were prepared by the reaction of phenyl carbamates with DEM in the presence of superacid catalysts.¹⁰ With two oxygens and a reactive methylene group, DEM is a very good substrate for carbonylation reactions. Thus, ethyl 2-ethoxyacetate was prepared by carbonylation of DEM using either Amberlyst 15¹¹ or Co₂(CO)₈/γ-picoline as catalyst.¹² Several phenylglycine derivatives and other amino acids were prepared by reacting DEM with anilines in the presence of carbon monoxide and a cobalt catalyst.¹³ In contrast to many of these applications, we feel that DEM has its greatest potential as a process solvent and reagent for organic chemistry, and we wish to report our investigations along those lines.

Synthesis and Properties

Diethoxymethane (DEM) is a colorless mobile liquid. There are several methods for preparing DEM, but the most economical route is by reacting formaldehyde and ethanol in the presence of an acid catalyst (Figure 1).

The typical properties of commercial diethoxymethane (DEM) are listed in Table 1.

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- (1) DEM is available in drum or tank car quantities from Eastman Chemical Company. Contact the author or call 1-800-EASTMAN for more details.
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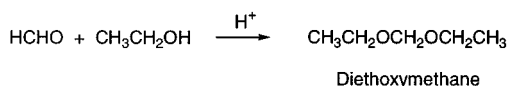


Figure 1.

Table 1

molecular formula:	C ₅ H ₁₂ O ₂
molecular weight:	104.15
appearance:	clear, colorless liquid
boiling point:	88 °C (190 °F)
freezing point:	-66.5 °C (-88 °F)
flash point:	-6 °C (21 °F)
viscosity at 20 °C:	0.405 cp
solubility (%):	
water in	1.3
in water	4.2
specific gravity at 20°/20 °C:	0.8305
vapor density (air = 1):	3.6
inhibitor (BHT), ppm:	100

Stability of Diethoxymethane

The stability of DEM is crucial for its use in process chemistry. Due to the nature and arrangement of functionality, it was important to examine the stability of DEM under basic, acidic, and oxidative conditions.

DEM is stable to numerous strong bases such as hydroxide, sodium hydride, Grignard reagents, and organolithium reagents (as will be described below). Being the diethyl acetal of formaldehyde, DEM is not stable under homogeneous acidic conditions for an extended period of time, and it is not recommended for use with homogeneous acid species as formaldehyde can be liberated under such conditions. However, DEM exhibits unexpected stability to aqueous acid, such that <1% of DEM is decomposed upon ambient temperature exposure to an equal volume of water at pH 2 over 24 h. This stability is attributed to the inherent hydrophobicity of DEM, which limits its exposure to the proton source. Thus, DEM is a useful solvent for reactions involving a mildly acidic work up, although it is recommended that the pH of an aqueous solution mixed with DEM remain at 4 or above.

Even though DEM is an ether, its propensity to form peroxides is very low compared to that of other ethers such as THF. As added insurance, DEM is commercially supplied with 100 ppm butylated hydroxytoluene (BHT) as a peroxide inhibitor.

Applications of Diethoxymethane

The applications of DEM can be best classified into two major categories: DEM as a solvent in organic processes and DEM as a chemical intermediate. Most of our investigations focused on the use of DEM as a solvent, but we will also present an example of its use as a reagent.

DEM as a Solvent

DEM has many properties that make it attractive as a general cost-competitive process solvent for use as a reaction medium and for operations such as extractions, dilutions, and recrystallizations. Its low viscosity allows easy handling. It forms a binary azeotrope with both water (90:10 DEM:

H₂O) at 75 °C and ethanol (58:42 DEM:ethanol) at 74 °C.¹⁴ These properties along with the immiscibility of DEM and water allow simple drying of DEM to very low water levels during recycling to afford good economics and a minimum of waste. DEM's freezing point (-66 °C) and boiling point (88 °C) offer a useful operating temperature range for many chemical sequences. Thus, DEM can potentially replace commonly used solvents such as tetrahydrofuran, ethyl acetate, dichloromethane, toluene, 1,4-dioxane, dimethoxyethane, *tert*-butyl methyl ether, and others. Indeed, DEM is currently used as a process solvent in various large-scale manufacturing settings. It has been evaluated for safety and handling properties and found to be suitable for industrial use.¹⁵

Two important characteristics of DEM which differentiate it from many other ethers are its water-immiscibility and its nonhygroscopic nature. It is manufactured in very dry form, with about 100–150 ppm water and includes 100 ppm butylated hydroxytoluene (BHT) peroxide inhibitor. In addition, it has very little propensity to absorb water. For example, DEM from a container that had been open for over a year performed superbly in our laboratories as a solvent for several water-sensitive reactions. Indeed, this is one of the most intriguing characteristic of DEM—it can readily be used for numerous water-sensitive reactions (even organometallic reactions) without any further drying. In addition, the water-immiscibility of DEM should facilitate product recovery as compared to solvents that are more water-miscible. We have compared DEM as manufactured (no further drying) with “anhydrous-grade” THF (stored under argon) as solvents for several representative organometallic reactions.

DEM has been compared with anhydrous THF for the benzylation of 3-butyne-1-ol using sodium hydride as base.¹⁶ Similar product yields were obtained in both cases, with product isolation much simpler with DEM due to its water-immiscibility (Figure 2a).

The reaction of benzaldehyde with *n*-butyllithium proceeded to slightly higher conversion in DEM than THF. The product isolation was again much simpler due to the water-immiscibility of DEM (Figure 2b).

A Grignard reaction, modeled in this case by the reaction of methylmagnesium chloride with benzaldehyde (Figure 2c), proceeded equally well in DEM and THF, with product isolation again being simpler from a DEM solution. However, we have found in our laboratories that the preparation of Grignard reagents appears to be more difficult in DEM than in other ethereal solvents.

The copper-catalyzed addition of methylmagnesium chloride to isophorone¹⁷ (Figure 2d) proceeded with higher selectivity (for the conjugate adduct) in DEM than in THF. In addition, the yield of product was significantly higher when the reaction was run in DEM.

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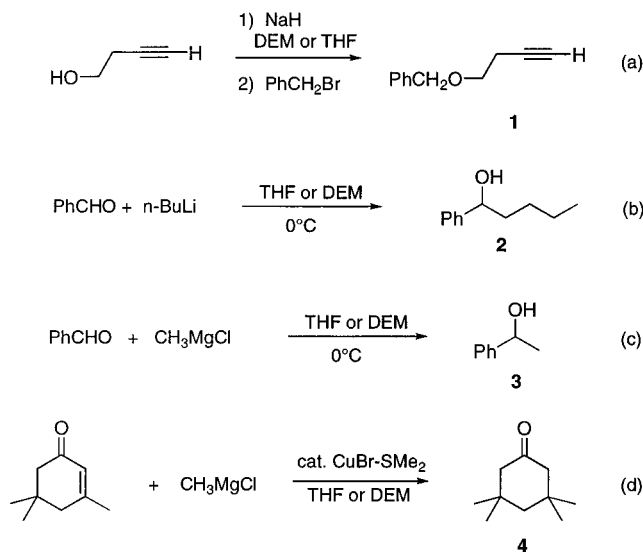


Figure 2.

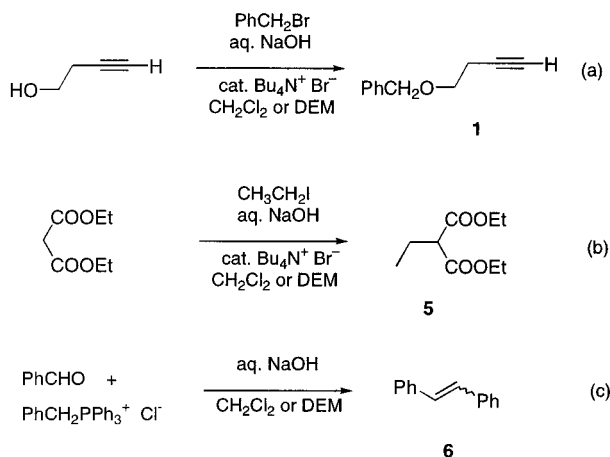


Figure 3.

These results indicate that in all of the organometallic reactions investigated DEM was equivalent or superior to anhydrous THF. We have also found DEM to be an attractive solvent for lithium dialkylcuprate conjugate addition reactions, palladium(0)-catalyzed allylation reactions, noble metal-catalyzed hydrogenations, and enzymatic esterification reactions.

DEM is also useful if a reaction warrants the presence of some water since DEM does have limited water solubility. Of particular interest were phase-transfer reactions. Although dichloromethane (DCM) is a standard solvent for phase-transfer-catalyzed reactions, concerns surround the use of this halogenated solvent. Thus, DEM was examined as a DCM replacement for phase-transfer reactions. Three different representative reactions were investigated: O-alkylation, C-alkylation, and a Wittig reaction (Figure 3). These reactions described below all employed aqueous sodium hydroxide as the base and, except for the Wittig reaction (where the reagent is the catalyst), tetrabutylammonium bromide was used as the catalyst.

The O-benzylation of 3-butyn-1-ol afforded similar reaction rates, yields, and product purities with either DCM or DEM as organic solvent (Figure 3a).

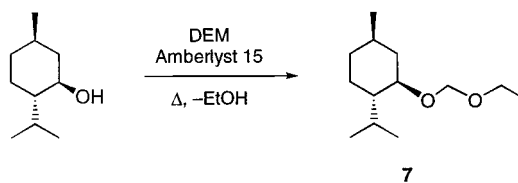


Figure 4.

Alkylation of diethyl malonate with ethyl iodide¹⁸ proceeded significantly faster in DEM than in DCM, with similar selectivities (Figure 3b).

The preparation of stilbene from benzaldehyde and benzyl triphenylphosphonium chloride¹⁹ proceeded at approximately the same rate and in similar yields in both DEM and DCM, with similar *E:Z* isomer selectivities (Figure 3c). In all of these cases product isolation was facilitated by the immiscibility of the aqueous and DEM layers.

DEM was an equivalent or superior solvent in all of the cases examined and is thus an attractive replacement solvent for DCM for phase-transfer-catalyzed reactions.

DEM as a Reagent

Due to the presence of its two oxygens, DEM has been found to be very useful in ethoxymethylation of alcohols, phenols,²⁰ and amines.²¹ Attaching an ethoxymethyl group is typically done using hazardous chloromethyl ethyl ether under basic conditions. DEM, however, can be used as an innocuous ethoxymethylating agent in the presence of an acidic catalysts. As an example, menthol was ethoxymethylated in quantitative yield using a solid acid catalyst with azeotropic removal of ethanol (Figure 4).

Conclusions

Diethoxymethane is finding wide acceptance as a reaction process solvent and for other applications in the chemical industry. In addition to its uses as a reagent, DEM shows particular promise as a solvent for reactions that are water-sensitive, mainly due to the low water content and non-hygroscopic nature of this diether solvent. DEM is also recommended as a solvent for phase-transfer-catalyzed reactions and for general processing of organic materials. The ease of handling, immiscibility with water, and ability for recycle serve to increase the attractiveness of this useful new solvent.

Experimental Section

General. Diethoxymethane (DEM) was commercial grade obtained from Eastman Chemical Company and in all cases was used as received. Other solvents and reagents were used as received from J. T. Baker Chemical Company or Aldrich Chemical Co. All ¹H- and ¹³C spectra were obtained on a Varian Gemini-300 spectrometer. Gas chromatography was

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performed on a Hewlett-Packard 5890 gas chromatograph using a J&W DB-17 (30 m × 0.25 mm) capillary column.

1-Benzyl-3-butyne (1) Prepared in DEM. A 60 wt % suspension of sodium hydride in mineral oil (1.00 g, 25 mmol, 1.0 equiv) was slurried in DEM (25 mL), and the mixture was cooled to 0 °C. 3-Butyne-1-ol (1.89 mL, 25 mmol) was added slowly dropwise with a small amount of frothing noted. The reaction mixture was warmed to ambient temperature for 15 min and then cooled to 0 °C. Benzyl bromide (2.82 mL, 23.75 mmol, 0.95 equiv) was added dropwise, and tetrabutylammonium iodide (462 mg, 1.25 mmol, 0.05 equiv) was added. The reaction mixture was allowed to warm to ambient temperature and stirred overnight to afford a white slurry. The mixture was quenched by careful addition of water (10 mL), and the layers were separated. The organic layer was dried (Na₂SO₄) and concentrated to afford 4.17 g of a 98:2 ratio of **1** and benzyl bromide, respectively. The crude product was flash-chromatographed and eluted with 2.5% ethyl acetate:heptane to afford 3.30 g (87%) of **1**. The analytical details were identical to those reported.¹³

1-Benzyl-3-butyne Prepared in THF. A 60 wt % suspension of sodium hydride in mineral oil (1.00 g, 25 mmol, 1.0 equiv) was slurried in THF (25 mL), and the mixture was cooled to 0 °C. 3-Butyne-1-ol (1.89 mL; 25 mmol) was added slowly dropwise with significant frothing noted. The reaction mixture was warmed to ambient temperature for 15 min and then cooled to 0 °C. Benzyl bromide (2.82 mL, 23.75 mmol, 0.95 equiv) was added dropwise, and tetrabutylammonium iodide (462 mg, 1.25 mmol, 0.05 equiv) was added. The reaction mixture was allowed to warm to ambient temperature and stirred overnight to afford a white slurry. The mixture was quenched by careful addition of water (10 mL), and the reaction mixture was diluted with a 1:1 mixture of ethyl acetate and heptane (50 mL). The layers were separated, and the organic layer was dried (MgSO₄) and concentrated to afford 4.28 g of a 98:2 ratio of **1** and benzyl bromide, respectively. The crude product was flash-chromatographed and eluted with a gradient of 0–10% ethyl acetate:heptane to afford 3.38 g (89%) of **1**.

1-Phenyl-1-butanol (2) Prepared in DEM. Benzaldehyde (1.06 g; 10 mmol) was dissolved in DEM (10 mL) in a dry, nitrogen-flushed flask. The solution was cooled to 0 °C, and a solution of *n*-butyllithium in hexane (2.5 M, 4.2 mL, 10.5 mmol, 1.05 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then quenched by the addition of water (10 mL). More DEM (20 mL) was added, and the layers were separated. The organic solution was dried (MgSO₄) and concentrated to afford 1.33 g of crude **2**. Examination of this material by ¹H NMR and GC indicated a 90:10 ratio of **2**:benzaldehyde. The **2** thus prepared was identical to an authentic sample.

1-Phenyl-1-butanol (2) Prepared in THF. Benzaldehyde (1.06 g, 10 mmol) was dissolved in THF (10 mL) in a dry, nitrogen-flushed flask. The solution was cooled to 0 °C, and a solution of *n*-butyllithium in hexane (2.5 M, 4.2 mL, 10.5 mmol, 1.05 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then quenched by the addition

of water (10 mL). Ethyl acetate (20 mL) was added, and the layers were separated. The organic solution was dried (MgSO₄) and concentrated to afford a crude product which still contained some water and salts. This material was dissolved in 25 mL of 1:1 ethyl acetate:heptane, dried (Na₂SO₄), and concentrated to afford 1.28 g of crude **2**. Examination of this material by ¹H NMR and GC indicated a 85:15 ratio of **2**:benzaldehyde.

1-Phenyl-1-ethanol (3) prepared in DEM: Benzaldehyde (1.06 g; 10 mmol) was dissolved in DEM (10 mL) in a dry, nitrogen-flushed flask. The mixture was cooled to 0 °C, and a solution of methylmagnesium chloride in THF (3.0 M, 3.33 mL, 10 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then warmed to ambient temperature for 1 h. The reaction was quenched by the addition of 3 N HCl (3.0 mL, 9.0 mmol, 0.9 equiv) and water such that the pH was about 6. The layers were separated, and the organic solution was dried (MgSO₄) and concentrated to afford 1.12 g (92%) of **3** which was identical to an authentic sample.

1-Phenyl-1-ethanol (3) Prepared in THF. Benzaldehyde (1.06 g, 10 mmol) was dissolved in THF (10 mL) in a dry, nitrogen-flushed flask. The mixture was cooled to 0 °C, and a solution of methylmagnesium chloride in THF (3.0 M, 3.33 mL, 10 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then warmed to ambient temperature for 1 h. The reaction was quenched by the addition of 3 N HCl (3.0 mL, 9.0 mmol, 0.9 equiv) and water such that the pH was about 6. The mixture was diluted with ethyl acetate (20 mL), and the layers were separated. The organic solution was dried (MgSO₄) and concentrated to afford 1.12 g (92%) of **3**.

3,3,5,5-Tetramethylcyclohexanone (4) Prepared in DEM. Copper bromide dimethyl sulfide complex (21 mg, 0.10 mmol, 0.1 equiv) was slurried in DEM (10 mL) and cooled to 0 °C. A solution of methylmagnesium chloride in THF (3.0 M, 4.0 mL, 12 mmol, 1.2 equiv) was added dropwise. The resulting mixture was warmed to ambient temperature for 15 min and then cooled to 0 °C. Isophorone (3,5,5-trimethylcyclohex-2-en-1-one) (1.50 mL, 10 mmol) was added dropwise to afford a gray suspension. The mixture was stirred for 30 min at 0 °C and then warmed to ambient temperature and allowed to stir overnight. The reaction mixture was treated with water (1 mL) and 3 M HCl (4.0 mL, 12 mmol; 1.2 equiv). The layers were separated, and the organic solution was dried (MgSO₄) and concentrated to afford 1.31 g (85%) of crude **4** which was 95.9% pure according to GC analysis (area %). The **4** thus produced was identical to an authentic sample.

3,3,5,5-Tetramethylcyclohexanone (4) Prepared in THF. Copper bromide dimethyl sulfide complex (21 mg, 0.10 mmol, 0.1 equiv) was slurried in THF (10 mL) and cooled to 0 °C. A solution of methylmagnesium chloride in THF (3.0 M, 4.0 mL, 12 mmol, 1.2 equiv) was added dropwise. The resulting mixture was warmed to ambient temperature for 15 min and then cooled to 0 °C. Isophorone (3,5,5-trimethylcyclohex-2-en-1-one) (1.50 mL, 10 mmol) was added dropwise to afford a gray solution. The mixture was

stirred for 30 min at 0 °C and then warmed to ambient temperature and allowed to stir overnight. The reaction mixture was treated with water (1 mL) and 3 M HCl (4.0 mL, 12 mmol, 1.2 equiv). Ethyl acetate was added, and the layers were separated. The organic solution was dried (MgSO₄) and concentrated to afford 1.18 g (77%) of crude **4** which was 91.2% pure according to GC analysis (area %).

1-Benzoyloxy-3-butyne (1) via Phase-Transfer Catalysis in DEM. 3-Butyn-1-ol (0.91 mL, 12 mmol, 1.2 equiv) was dissolved in 5 mL of DEM. Benzyl bromide (1.19 mL, 10 mmol) was added followed by tetrabutylammonium bromide (161 mg, 0.50 mmol, 0.05 equiv). Water (1 mL) was added followed by sodium hydroxide (2.00 g, 25 mmol, 2.5 equiv). The resulting mixture was stirred for 1.5 days at ambient temperature to completely consume benzyl bromide according to GC analysis. The reaction mixture was diluted with DEM, and the layers were separated. The resulting organic solution was washed with water (5 mL), dried (MgSO₄), and concentrated to afford 1.60 g (99%) of **1** with no detectable impurities (¹H NMR analysis).

1-Benzoyloxy-3-butyne (1) via Phase-Transfer Catalysis in DCM. 3-Butyn-1-ol (0.91 mL, 12 mmol, 1.2 equiv) was dissolved in 5 mL of dichloromethane. Benzyl bromide (1.19 mL, 10 mmol) was added followed by tetrabutylammonium bromide (161 mg, 0.50 mmol, 0.05 equiv). Water (1 mL) was added followed by sodium hydroxide (2.00 g, 25 mmol, 2.5 equiv). The resulting mixture was stirred for 1.5 days at ambient temperature to completely consume benzyl bromide according to GC analysis. The reaction mixture was diluted with ethyl acetate, and the layers were separated. The resulting organic solution was washed with water (5 mL), dried (MgSO₄), and concentrated to afford 1.63 g (99%) of **1** with no detectable impurities (¹H NMR analysis).

Diethyl 2-Ethylmalonate (5) via Phase-Transfer Catalysis in DEM. Diethyl malonate (1.52 mL, 10 mmol) was dissolved in DEM (5 mL). Iodoethane (1.6 mL, 20 mmol, 2.0 equiv) was added followed by tetrabutylammonium bromide (161 mg, 0.50 mmol, 0.05 equiv). Water (1 mL) was added followed by 50% sodium hydroxide (1.60 g, 20 mmol, 2.0 equiv). The reaction mixture was stirred at ambient temperature and assayed by GC. After 1 h, 94% consumption of diethyl malonate was observed with a 99:1 ratio of **5** to dialkylated malonate. After the mixture stirred overnight at ambient temperature, complete consumption of diethyl malonate was observed with a ratio of **5** to dialkylated material of 94:6. The mixture was neutralized to pH 7 by the addition of aqueous HCl. The layers were separated, and the organic layer was dried (MgSO₄) and concentrated to afford **5** which was contaminated with dialkylated material. The **5** thus produced was identical to an authentic sample.

Diethyl 2-Ethylmalonate (5) via Phase-Transfer Catalysis in Dichloromethane. Diethyl malonate (1.52 mL,

10 mmol) was dissolved in dichloromethane (5 mL). Iodoethane (1.6 mL, 20 mmol, 2.0 equiv) was added followed by tetrabutylammonium bromide (161 mg, 0.50 mmol, 0.05 equiv). Water (1 mL) was added followed by 50% sodium hydroxide (1.60 g, 20 mmol, 2.0 equiv). The reaction mixture was stirred at ambient temperature and assayed by GC. After 1 h, 71% consumption of diethyl malonate was observed with a >99:1 ratio of **5** to dialkylated malonate. After the mixture stirred overnight at ambient temperature, complete consumption of diethyl malonate was observed with a ratio of **5** to dialkylated material of 99:1.

1,2-Diphenylethylene (6) in DEM. Benzyl triphenylphosphonium chloride (7.78 g, 20 mmol, 1.0 equiv) and benzaldehyde (2.03 mL, 20 mmol) were combined in 10 mL of DEM. Aqueous sodium hydroxide (50%, 10 mL, excess) was added, and the resulting mixture was stirred vigorously at ambient temperature for 3 h. The reaction mixture was diluted with DEM and washed with water, dried over magnesium sulfate, and concentrated. The crude product (6.76 g) was filtered through a pad of flash silica gel and eluted with 1:4 ethyl acetate:heptane to afford 3.40 g (94%) of **6** as a 55:45 *E:Z* ratio of isomers. *E*- and *Z*-**6** were identical to authentic samples.

1,2-Diphenylethylene (6) in Dichloromethane. Benzyl triphenylphosphonium chloride (7.78 g, 20 mmol, 1.0 equiv) and benzaldehyde (2.03 mL, 20 mmol) were combined in 10 mL of DEM. Aqueous sodium hydroxide (50%, 10 mL, excess) was added, and the resulting mixture was stirred vigorously at ambient temperature for 3 h. The reaction mixture was diluted with DEM and washed with water, dried over magnesium sulfate, and concentrated. The crude product (8.90 g) was filtered through a pad of flash silica gel and eluted with 1:4 ethyl acetate:heptane to afford 3.49 g (97%) of **6** as a 46:54 *E:Z* ratio of isomers.

Ethoxymethylmenthol (7). Menthol (3.91 g, 25 mmol) was dissolved in DEM (25 mL). Amberlyst 15 acidic resin (196 mg, 5 wt %) was added, and the reaction mixture was heated to reflux for 2 h to consume about 80% of the menthol (GC analysis). Most of the volatiles were removed between 65 and 85 °C to afford a 95:5 mixture of **7**:menthol. DEM (10 mL) was added, and the volatiles were azeotropically distilled for 1 h at which point GC analysis indicated >99% conversion. The reaction mixture was filtered, and solvent was removed to afford 5.38 g (99%) of **7** which was >99% pure by GC analysis. ¹H NMR (CDCl₃) δ 4.827 (d, 1H, *J* = 7.14 Hz); 4.639 (d, 1H, *J* = 7.14 Hz); 3.7–3.5 (m, 2H); 3.366 (dt, 1H, *J* = 4.21, 10.50 Hz); 2.2 (m, 1H); 2.083 (br d, 1H, *J* = 12.09 Hz); 1.7–1.6 (m, 2H); 1.4 (m, 1H); 1.216 (t, 3H; 7.08 Hz); 0.911 (d, 6H, *J* = 6.78 Hz); 1.1–0.8 (m, 4H); 0.779 (d, 3H, *J* = 7.08 Hz).

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